NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

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THE SYNTHESIS AND PURIFICATION OF AROMATIC HYDROCARBONS

II - 1,2,4-TRIMETHYLBENZENE

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SUMMARY

A new method for the synthesis and purification of a 14-gallon quantity of 1,2,4-trimethylbenzene is described. This method consists in the chloromethylation of m- and p-xylenes, subsequent formation of ethyl dimethylbenzyl ethers, and hydrogenolysis of the ethers to yield the hydrocarbon. A yield of 35 percent was obtained from a mixture of m- and p-xylenes and a 25-percent yield was obtained from commercial xylenes. Physical properties of the "best" gallon and of the engine sample of 1,2,4-trimethylbenzene are given. Evidence is presented for the existence of two crystalline modifications of 1,2,4-trimethylbenzene.

INTRODUCTION

The synthesis and purification of 1,2,4-trimethylbenzene was undertaken in conjunction with a program that is being conducted at the Cleveland laboratory of the NACA on the study of aromatic hydrocarbons as possible components of aviation gasoline. The synthesis of n-butylbenzene is reported in part I (reference 1).

Only two of the methods reported in the literature for the synthesis of 1,2,4-trimethylbenzene were considered to produce the hydrocarbon sufficiently free of its isomers to be readily purified for engine tests. Smith and Lund (reference 2) reported a 37-percent yield from 2,4-dimethylaniline. The method reported by these authors involved the preparation of 2,4-dimethyliodobenzene by diazotization of the amine followed by addition of potassium iodide to the diazonium salt solution. From the 2,4-dimethyliodobenzene, 2,4-dimethylphenylmagnesium iodide was prepared and condensed with dimethyl sulfate. Maxwell and Adams (reference 3) synthesized the hydrocarbon from 2,4-dimethylbromobenzene (obtained from bromination of pure m-xylene)

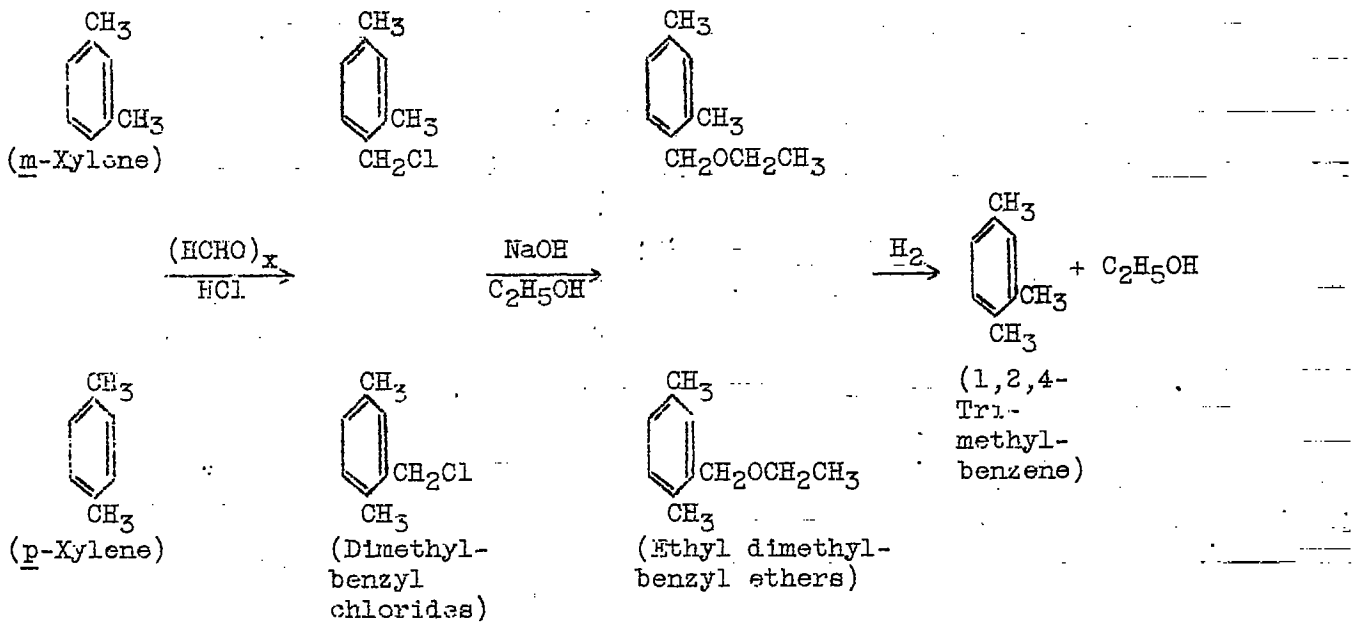
in a similar manner by condensing dimethyl sulfate with the Grignard reagent. Because the starting materials were unavailable in sufficient quantities, neither of these methods appeared suitable for large-scale synthesis of the hydrocarbon.

A new method for the synthesis and purification of 14 gallons of 1,2,4-trimethylbenzene from readily available starting materials is described herein. In brief, the synthesis consists in the chloromethylation of xylenes, the conversion of dimethylbenzyl chlorides obtained to the corresponding ethyl dimethylbenzyl ethers, and the hydrogenolysis of the ethers to 1,2,4-trimethylbenzene. The physical properties of the hydrocarbons are given, and evidence is presented for the existence of two crystalline modifications of 1,2,4-trimethylbenzene. This work was completed in April 1944.

DISCUSSION OF SYNTHESIS

Chloromethylation of m- and p-xylenes according to the method described in reference 4 gave good yields (60 to 65 percent) of 2,4- and 2,5-dimethylbenzyl chlorides. Exploratory work indicated that the replacement of the chlorine atom by an atom of hydrogen could be successfully accomplished in two ways to yield the desired 1,2,4-trimethylbenzene. Slow addition of the dimethylbenzyl chlorides, diluted with 6 parts of an inert solvent, to sodium dissolved in liquid ammonia gave from 60- to 65-percent conversion to 1,2,4-trimethylbenzene. Although this method gave a good product and yield, it was time-consuming because suitable equipment for handling large quantities of liquid ammonia was unavailable.

Another method, and the one chosen for large-scale synthesis, involved the treatment of the isomeric dimethylbenzyl chlorides with alcoholic sodium hydroxide to produce the corresponding ethyl dimethylbenzyl ethers. High-pressure hydrogenolysis at elevated temperatures over copper chromite hydrogenation catalyst cleaved the ethers to give 1,2,4-trimethylbenzene and ethyl alcohol from both isomers. (See reference 5.) The method of synthesis may be summarized schematically as follows:



The first chloromethylation run was made using a mixture of m- and p-xylenes obtained from one distillation of commercial xylenes through a 2-inch by 26-foot modified stainless-steel Fenske column of 100 theoretical plates. A 2° cut (137° to 139° C) was taken as starting material. On subsequent runs commercial xylenes were used directly from the drum without further purification. The only observed difference between the first and the subsequent runs was a decrease in the yield of the dimethylbenzyl chlorides obtained from chloromethylation of the xylenes. This decrease in yield was undoubtedly due to the high-boiling material (15 to 20 percent) in the commercial xylenes. When unpurified commercial xylenes were used as starting material, the over-all yield of 1,2,4-trimethylbenzene was reduced from 35 to 25 percent of the theoretical.

Since it is theoretically possible for the chloromethylation of m- and p-xylenes to yield three isomeric dimethylbenzyl chlorides, which give rise to three trimethylbenzenes, care was taken in the purification of the 1,2,4-trimethylbenzene. A single distillation of the crude product of hydrogenolysis through a modified Fenske column of 100 theoretical plates gave the distillation and the refractive index curves shown in figure 1. These curves show no evidence of 1,3,5-trimethylbenzene and from 2 to 3 percent of 1,2,3-trimethylbenzene. The 1,2,3-trimethylbenzene was easily removed by fractional distillation. The physical properties of the three trimethylbenzenes, presented in the following table, indicate that the isomeric trimethylbenzenes can be detected and separated from the 1,2,4-trimethylbenzene.

Compound	Source	Freezing point (°C)	Boiling point (°C)	Index of refraction n_D^{20}	Density at 20° C (grams/ml)
1,2,4-Trimethylbenzene	Cleveland laboratory	-44.00	169.4	1.5048	0.8757
1,2,3-Trimethylbenzene	Reference 6	-25.4	176.1	[a]1.5107	.8951
1,3,5-Trimethylbenzene	Reference 6	-44.7	164.6	1.4991	.8653

[a]At 25° C.

The 1,2,4-trimethylbenzene was further purified by two more fractionations through a column of 100 theoretical plates. Neither the boiling point nor the index of refraction was changed but the freezing point was raised 0.2° C. The physical properties of the "best" sample and of the engine sample prepared at the Cleveland laboratory are given in the following table together with properties reported in reference 6:

Compound	Source	Freezing point (°C)	Boiling point at 760 mm (°C)	Refractive index n_D^{20}	Density at 20° C (grams/ml)
1,2,4-Trimethylbenzene (engine sample)	Cleveland laboratory	-44.22	169.3	1.5048	0.8757
1,2,4-Trimethylbenzene ("best" sample)	Cleveland laboratory	-44.00	169.4	1.5048	.8757
1,2,4-Trimethylbenzene	Reference 6	-44.05	169.18	1.5048	.8762

Part of the best sample prepared at Cleveland was sent to the National Bureau of Standards for further purification and determination of physical properties under the direction of Dr. F. D. Rossini. The material as received was reported to be 99.59 ±0.20 mole percent pure. It was further purified at the National Bureau of Standards to a purity of 99.71 ±0.20 mole percent. The calculated freezing point for pure 1,2,4-trimethylbenzene was reported to be -43.80 ±0.07° C.

Figure 2 shows the freezing curve for the best sample of 1,2,4-trimethylbenzene obtained at the Cleveland laboratory. The curve indicates nonequilibrium conditions. Most of the freezing curves obtained at this laboratory for this aromatic hydrocarbon have been similar, and the same difficulty has been noted in the literature. (See reference 7.)

Inasmuch as the 1,2,3- and the 1,3,5-trimethylbenzenes have been found to form more than one crystalline modification (reference 8), an attempt was made to obtain more than one crystalline modification of the 1,2,4-trimethylbenzene. Figure 3 shows the freezing curves obtained when the hydrocarbon was cooled with and without seeding until crystallization occurred. The existence of two distinct plateaus (approximately 5° C apart) in the curve obtained without seeding indicates that two crystalline modifications exist and that the lower-melting form is the least stable of the two.

EXPERIMENTAL DETAILS

A 14-gallon quantity of 1,2,4-trimethylbenzene was prepared according to the reactions previously outlined. Typical quantities of the reactants and yields of the products are given in the following discussion.

Chloromethylation of xylene. - In a 30-gallon glass-lined reactor equipped with stirrer, gas-delivery tube, and reflux condenser connected to a water aspirator, 15.9 kilograms (147 moles) of the distilled xylenes (137° to 139° C), 10 gallons of technical hydrochloric acid (conc.), and 3.5 kilograms (121 moles) of paraformaldehyde were mixed with vigorous stirring. The mixture was heated to a temperature of 50° to 60° C by passing hot water through the jacket of the reactor. Then 7.9 kilograms (217 moles) of anhydrous hydrogen chloride was slowly bubbled through the mixture over a period of 12 hours while a temperature of 50° to 60° C and vigorous stirring were maintained.

At the end of 12 hours, the mixture was cooled to room temperature and the acid layer drawn off. The same 10 gallons of concentrated hydrochloric acid was used for each run. The oil layer was then washed twice with water and once with a saturated solution of sodium bicarbonate. The dimethylbenzyl chlorides obtained from chloromethylation were highly lachrymatory and care was used in handling them. No attempt was made to separate the product from the unreacted xylenes at this stage.

Conversion of dimethylbenzyl chlorides to ethyl dimethylbenzyl ethers. - In a stainless-steel reactor, equipped with stirrer, reflux condenser, and dropping funnel, 5.4 kilograms (136 moles) of technical sodium hydroxide was added slowly to 4 gallons of ethyl alcohol. Care was taken to keep the temperature below 70° C. The dimethylbenzyl chloride-xylene mixture was added slowly to the alcoholic sodium hydroxide solution, while continuous agitation was maintained. The rate of addition was adjusted to maintain gentle refluxing of the ethyl alcohol. From 4 to 5 hours were required to add the dimethylbenzyl chloride-xylene mixture, after which the mixture was stirred under reflux for an additional 4 hours. At the end of this period a sample was withdrawn, washed free of chloride salts, and tested for halides by the Beilstein copper oxide method.

The presence of even small traces of chlorides in the ethyl dimethylbenzyl ethers poisoned the hydrogenation catalyst. The presence of chlorides also led to polymerization of the ethyl dimethylbenzyl ethers at the high temperatures reached during distillation. The presence of copper or copper salts at temperatures as low as 80° to 120° C led to polymerization of the dimethylbenzyl chlorides with the evolution of hydrogen chloride gas. For these reasons care was taken to have the ethyl dimethylbenzyl ethers free of chlorides before attempting distillation.

In case the material still contained chlorides, additional sodium hydroxide was added and the treatment was continued until all traces were removed. The reflux condenser was then changed for downward distillation and the excess ethyl alcohol distilled. The remaining oil was washed with water until free of sodium chloride and unreacted sodium hydroxide, and distillation was continued. The fraction distilling between 218° and 235° C was considered to be ethyl dimethylbenzyl ether. The yield of the crude ethers was 65 percent of the theoretical, based on paraformaldehyde as the limiting factor. A small amount of high-boiling residue was left in the distillation pot. This high-boiling material was thought to be a mixture of polyethers resulting from the conversion of polychloromethyl xylenes. No attempt was made to verify this supposition.

A small sample of the isomeric ethers was further purified by fractional distillation through a 3-foot packed column for purposes of identification. The boiling point of the isomeric mixture was 221° to 222° C at 750 millimeters of mercury. No attempt was made to separate the isomers, but a carbon and hydrogen analysis was run on the fractionated material. Analysis – Calculated for $C_{11}H_{16}O$: C, 80.49 percent; H, 9.75 percent. Found: C, 79.47, 79.46 percent; H, 9.79, 9.76 percent.

Hydrogenolysis of the ethyl dimethylbenzyl ethers. - The crude ethyl dimethylbenzyl ethers were converted by hydrogenolysis to 1,2,4-trimethylbenzene. This hydrogenolysis was carried out in a 20-liter bomb using 4.3 kilograms of the ethers and 150 grams (3 percent by weight) of copper chromite hydrogenation catalyst. Hydrogen was added to an initial pressure of 1500 pounds per square inch at 25° C and the bomb was heated to 300° C as rapidly as possible; maximum pressure reached during the run was 2900 pounds per square inch. The reactants were held at 300° C with continuous agitation for a period of 6 hours. The heaters were then turned off and the bomb cooled by blowing air between the heating jacket and the bomb.

After the bomb had cooled to room temperature, the excess hydrogen was exhausted, the product removed, and the catalyst separated by filtration. Three runs were required to cleave the ethers produced from the conversion of the dimethylbenzyl chlorides. The product was distilled through a 2-inch by 12-foot modified Fenske column of 40 theoretical plates. The fraction boiling between 167.0° and 168.5° C at 745 millimeters of mercury was then distilled twice through a 2-inch by 26-foot modified Fenske column of 100 theoretical plates. The yield of 1,2,4-trimethylbenzene was 60 percent of the theoretical based on the crude ethyl dimethylbenzyl ethers.

Identification of byproducts. - Distillation of the product of hydrogenolysis gave from 23 to 25 percent by weight of material distilling at 78° to 80° C. This material was identified as ethyl alcohol by a positive iodoform test and a 3,5-dinitrobenzoate derivative with a melting point of 92.5° to 93° C. A mixture of the 3,5-dinitrobenzoate derivative with an authentic sample of this material gave no lowering of the melting point Quantitative analysis of this low-boiling fraction by the acetylation method described in reference 9 indicated that at least 90 percent of the material was ethyl alcohol. Calculations on a molar basis showed that within experimental error 1 mole of ethyl alcohol was obtained for each mole of hydrogenated product. This fact was taken as further evidence that the product obtained from the dimethylbenzyl chlorides was the corresponding ethyl dimethylbenzyl ethers.

Analysis of the high-boiling distillation residue showed that a small amount of 1,2,4,5-tetramethylbenzene (durene) was also produced. This product was separated from the oil by crystallization and was purified by recrystallization from aqueous ethyl alcohol. The melting point of the pure material was 79° to 80° C. The 3,6-dinitro derivative of the hydrocarbon melted at 204° to 205° C after recrystallization from ethyl alcohol. The melting points

reported in reference 10 are 79° C for durene and 205° C for its dinitro derivative. The presence of durene was attributed to dichloromethylation of the xylenes and failure to purify the ethers before hydrogenolysis.

The remaining high-boiling material was completely soluble in cold concentrated sulfuric acid and gave no test for unsaturation, indicating that it was aromatic in nature. No further attempt was made to characterize this material.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, August 23, 1945.

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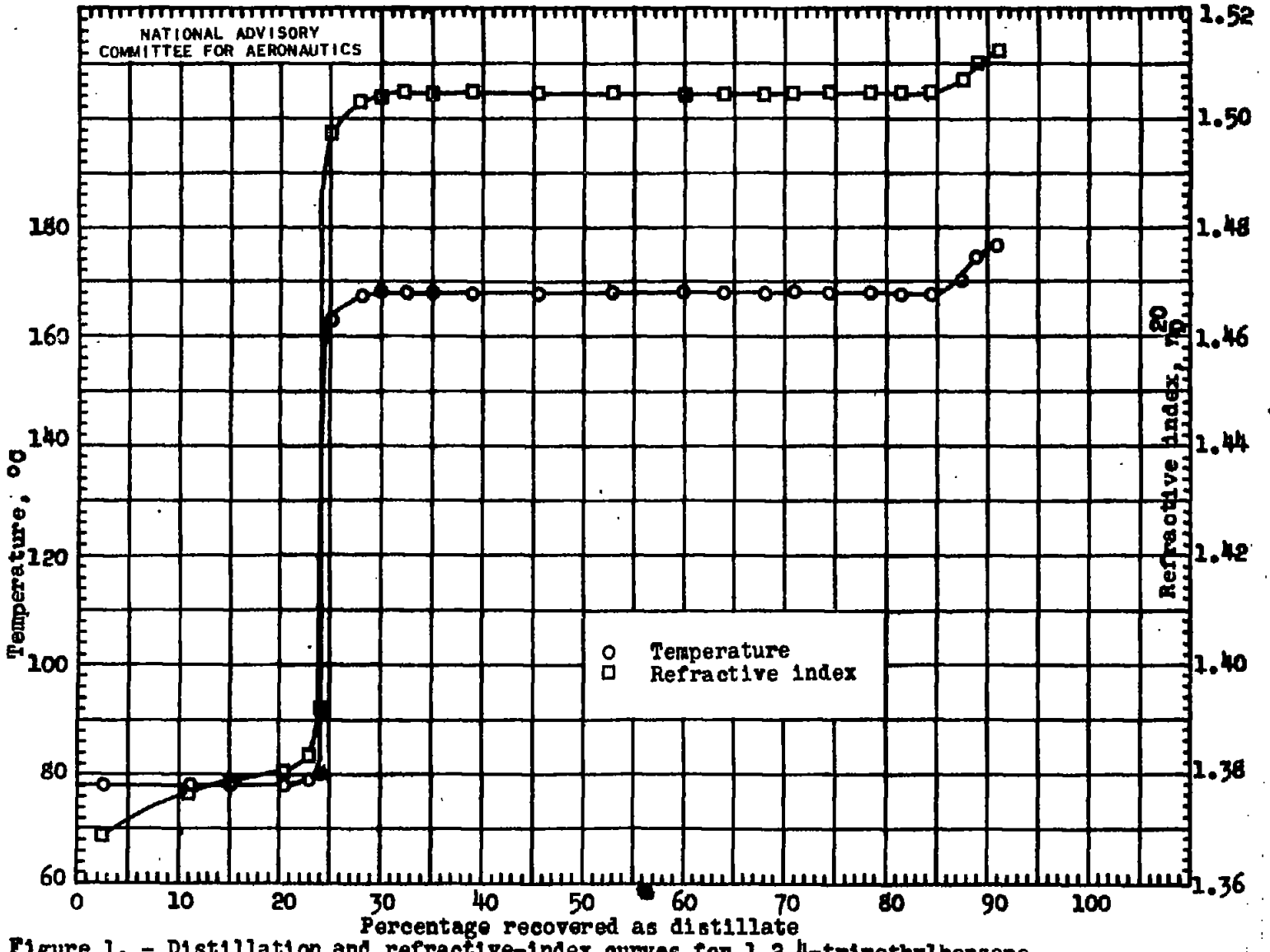

Figure 1. - Distillation and refractive-index curves for 1,2,4-trimethylbenzene.

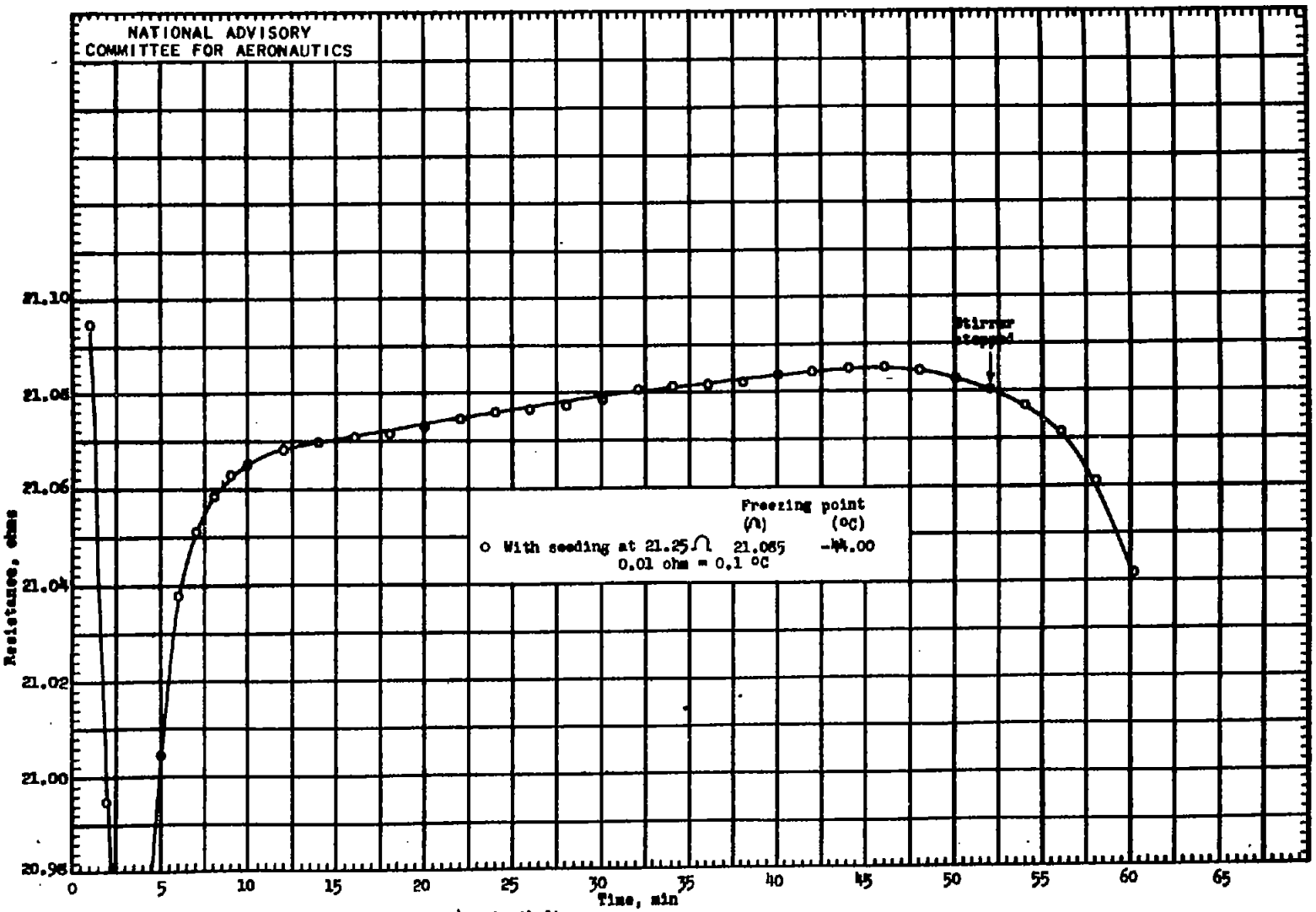

Figure 2. - Freezing curve of best sample of 1,2,4-trimethylbenzene.

Fig. 2

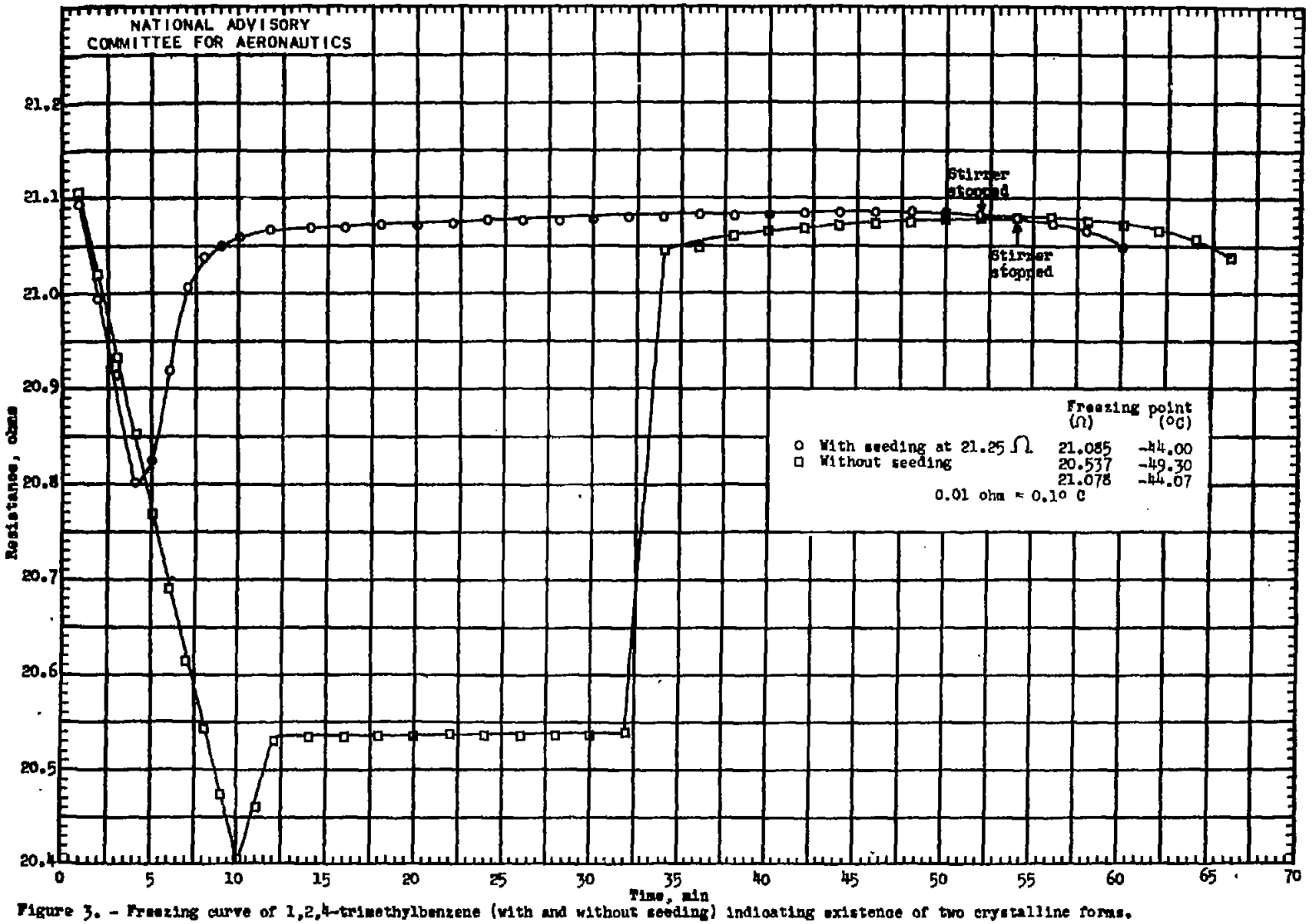

Figure 3. - Freezing curve of 1,2,4-trimethylbenzene (with and without seeding) indicating existence of two crystalline forms.